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THE MÖSSBAUER EFFECT: A HIGH RESOLUTION PROBE OF THE INTERIOR OF MATERIALS

by

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ABSTRACT

The nature of the Mössbauer effect is explained using a simple physical picture. The application of this technique to iron pyrite, FeS_2, is discussed. Some of the equipment used for these experiments is described.

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Various fields of research in the disciplines of chemistry and physics may be clearly deliniated by the energies involved in the processes under study. Nuclear physics is concerned with events whose energies are generally greater than 10 kiloelectron volts (keV), while the chemist and solid state physicist are primarily interested in those events which involve energies between 1 and 10 electron volts (eV). The research worker interested in lattice vibrations is concerned with energies between 10^{-2} and 10^{-1} electron volts, and low temperature physics deals with 10^{-4} electron volt processes. There has been very few experimental situations which involve two or more of these energy regions. Some exceptions are the use of perturbed angular correlations (1) and positron annihilation (2) (both nuclear physics phenomena) to study certain properties of solids. Recently the discovery by R.L. Mossbauer (3) of the recoilless emission of gamma rays by nuclei bound within materials is another example

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of coupling between nuclear physics and the solid state.

In Figure 1 is a plot of the various energy regions which are of interest to scientific workers. It is seen that there is an overlap of the lattice vibration and chemical binding energies and the free atom recoil energy of low-energy gamma rays. It is these gamma rays which are capable of giving rise to the Mössbauer effect. There are several interesting things to notice with respect to this Figure. First, the extremely narrow width of gamma-ray lines as compared with their energy, and secondly the narrowness of these lines as compared with the lattice vibration and chemical bonding energies. Thus, if one had a probe with an inherent line width equal to that of a nuclear gamma ray, extremely detailed studies of the nature of the energies involved in chemical binding would be possible. Such a probe is provided by the Mössbauer effect.

Now exactly what is this Mössbauer effect which is capable of such energy resolutions? Let us first briefly review some of the properties of resonance absorption so that the Mössbauer effect may be fitted into this general pattern. In order to achieve resonance absorption for electromagnetic radiation, the energy of the emitted photon must lie within the energy of the absorbing states; that the emission and absorption energies are not the same is due to the effect of recoil. Both the emitter and absorber must recoil with an energy such that momentum is conserved. If the sum of these two recoil energies is greater than the inherent line width of the emitting spectrum, no resonant absorption will occur. The

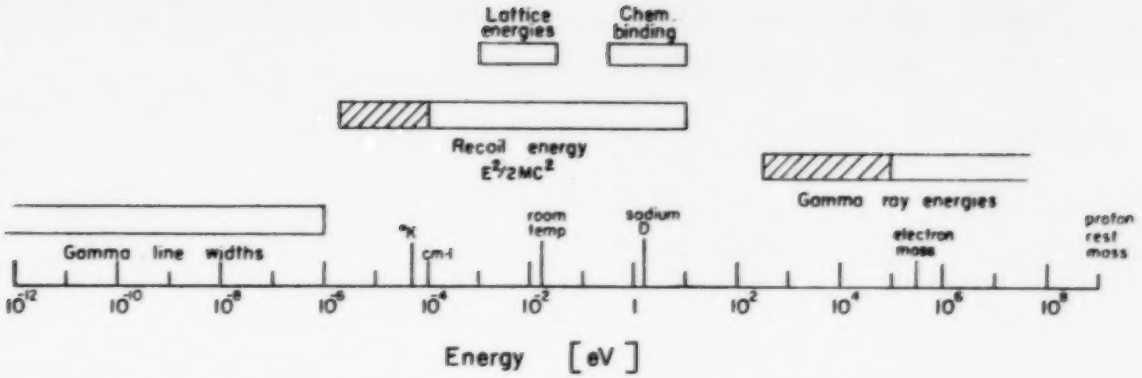
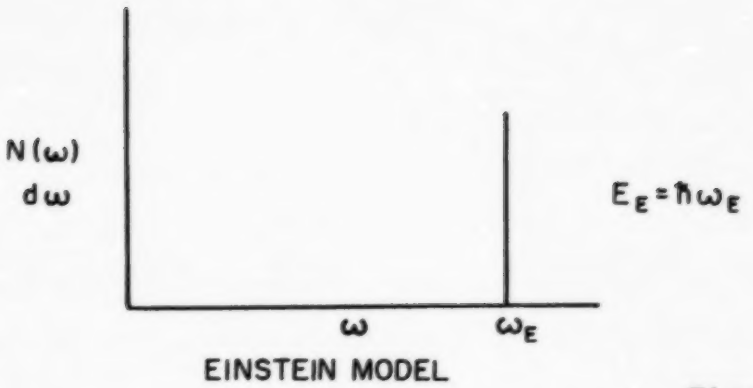


Figure 1 - A logarithmic plot having energies of various phenomena encountered in nature.



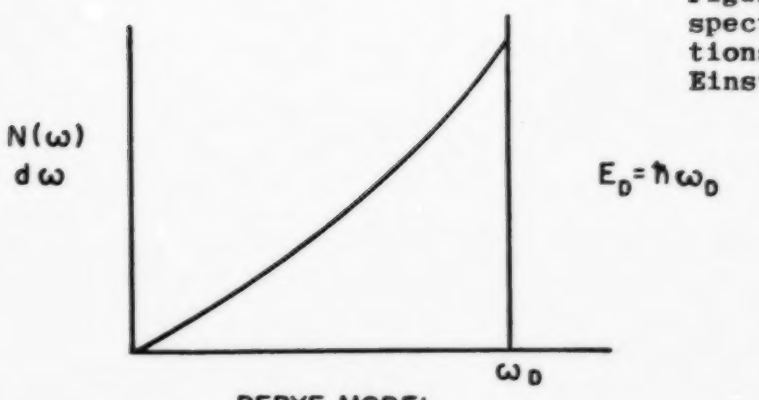


Figure 2 - The frequency spectra of lattice vibrations. Both the Debye and Einstein model are shown.

formula for the recoil energy, R, is:

$$R = \frac{E^2}{2Mc^2}$$

where E is the transition energy in eV

$2Mc^2$ is the rest mass expressed in energy units Eq 1)

Thus if E is large or M is small, the recoil energy will be large.

In the case of optical transitions, the energy is a few electron volts and the mass is essentially the mass of an atom, which is in the order of 1 GeV (giga electron volts = 10^{-9} eV). From equation 1, therefore, the recoil energy is 5×10^{-10} eV. The line width Γ may be calculated from the uncertainty principle

$$\Gamma \ \Delta t \ \geq \ \hbar$$

where Γ is the line width

Δt is the life time

$\hbar$ is Plancks' constant divided by 2π Eq 2)

or $$\Gamma \geq \frac{6 \times 10^{-16} \text{ eV}}{\Delta t}$$ Eq 3)

For an optical transition with a mean life of 10^{-8} sec., the line width is 6×10^{-8} eV. Resonance absorption will occur and is typified by the familiar Fraunhofer absorption lines of the sun's spectrum.

In the case of the nuclear emission of gamma rays, the energy E is a few kiloelectron volts or more while the mass M remains essentially the same as for the optical situation.

In the case of nuclear events, resonant fluorescent absorption is extremely rare. An excellent review article by Malmfors (4) describes these experiments.

The Mössbauer effect is a nuclear phenomenon which involves the properties of the solid state of matter. The requirement for resonance is that the recoil energy, R, be less than the line width, Γ . For nuclear events this is in general not true. In order to achieve resonant absorption: either one can make up the recoil energy by some external means (such as a Doppler shift), or, one can reduce the recoil energy by either decreasing the energy of the transition or increasing the effective mass. Because the energy of a transition is fixed by the properties of the states involved, the only way to achieve resonant absorption is to increase the effective mass of the system. In a solid, if the average recoil energy per atom is less than the energy required to excite one or more phonons, the atom will appear to be bound and have an effective mass equal to the total mass of the system. This increase in mass will result in the transition being recoilless and hence resonant absorption can occur. Such a recoilless transition is known as a Mössbauer transition.

In order to see that this is reasonable, let us examine two simple models of lattice vibrations shown in Figure 2. The simplest model is that proposed by Einstein, where lattice vibrations are described as oscillators, all having an equal energy E_E. If the total recoil energy R is less than E_E, no phonon excitation can occur and the emitted

gamma ray will have its full energy. This model is not very realistic; a more realistic model, as proposed by Debye, will exhibit the same recoilless emission of gamma rays. The Debye model predicts a continuum of energy from zero energy up to a maximum E_D. The high energy spectrum is due to those atoms which are moving in destructive interference with respect to their neighbours and the low energy spectrum is due to those atoms which are moving in constructive interference with respect to their nearest neighbours. This latter phenomenon involves the motion of one or more mass centres and hence again we see the increasing of mass when the atom is bound in the solid.

The probability of such recoilless emission obviously depends on the lattice energies which are excited. This in turn, of course, is a function of the temperature of the material. Hence, for low temperatures, where most of the available states are filled, the fraction of recoilless emission is high, but, for high temperatures, where there is a broad spectrum of available states, the recoilless fraction is low. The expression for the recoil-free fraction, f, may be written as

$$f \propto e^{-\langle x^2 \rangle} \qquad \text{Eq 4)}$$

where $\langle x^2 \rangle$ is the mean square amplitude of vibration in the direction of the emission of the gamma ray. The averaging time for this is the lifetime of the nuclear level involved in the gamma emission process. This mean amplitude of vibration implies that the nucleus is, in fact, involved in a bounded

situation so that the average value of oscillation amplitude is small.

In the case of a liquid, where the mean square amplitude of vibration is not bounded, there will be no Mössbauer effect. However, as the viscosity of the liquid increases (for example glycerol (5)) a Mössbauer effect has been observed. By measuring the recoilless fraction in various directions along the crystal axes, anisotropies in the mean square amplitude of vibration may be detected. This effect has been observed in oriented single crystals (6) as will be shown later.

Thus in the Mössbauer effect we have an extremely fine probe of the effects of the external solid state fields on the nucleus. These effects may be characterized in three classes: isomer shift or electric monomer effect; magnetic hyperfine structure due to the magnetic dipole - magnetic field interaction; and electric hyperfine splitting due to the quadrupole moment of the nucleus interacting with the electric field gradient.

THE ISOMER SHIFT

The Mössbauer effect allows an accurate measurement of the difference in energy between the same nuclear state in different electromagnetic environments. Since the nucleus is of finite size and there is a probability of the s electrons penetrating within the nuclear volume, this electronic charge

will interact with the nuclear levels. The energy of this interaction can be computed by considering a uniformerly charged nucleus imbedded in an s electron environment. A change in the s electron density may arise from a change in the valence of the system which manifests itself as a shift in the nuclear energy level. This effect may be considered as an electric monopole interaction.

The isomer shift is extremely important in that it yields information that is not readily available from any other type of experiment. This information gives direct evidence concerning the various types of chemical bonding. The measurement of the electronic charge density at the nucleus is sensitive directly to the s electrons and indirectly to the other electrons which may be involved in the chemical bonds. The s electron density is extremely sensitive to the unfilled shells such as occur in the lanthanide and actinide series and also to the 3d electrons as found in transition metals. There is a large difference between the isomer shift for an Fe^{2+} (1.4 mm per sec) and an Fe^{3+} (0.4 mm per sec) ion. Thus using a study of the isomer shift with the Mössbauer effect, it is possible to determine the charge states of the ions within a material and the ionic character of the bond (7). This has proved an invaluable tool for elucidating the various properties of tin organic compounds and also the pi-bonding systems, especially cyclo-pentadienyl-iron and cyclo-octatetraene-iron compounds (8).

MAGNETIC HYPERFINE SPLITTING

The magnetic dipole moment of the nucleus is capable of interacting with the magnetic fields produced by the surrounding atoms and the resulting magnetic hyperfine structure has been extremely useful in the study of magnetism. It has made possible a detailed study of the ferromagnetic exchange interactions in iron (9) and has led to a better understanding of the properties of ferromagnetism. Using the rare-earth Mössbauer isotopes, the rare-earth iron garnets (10) and the cubic Laves-phase compounds (11) have been extensively studied. Some of these materials are ferrimagnetic and much information concerning ferrimagnetism has been obtained from Mössbauer experiments.

ELECTRIC HYPERFINE SPLITTING

The interaction of the nuclear quadrupole moment with the electric field gradients as produced by surrounding ions has allowed the measurement of several quadrupole interactions. Fundamental sources of the electric field gradient are changes from distant ions and the electrons of incompletely filled shells of the atoms which are exhibiting the Mössbauer effect. The crystal structure is known to a high degree of precision and if the effective ionic charge can be assigned to the various lattice sites, the value of the electric field gradient at the atomic site can be easily calculated. However, the

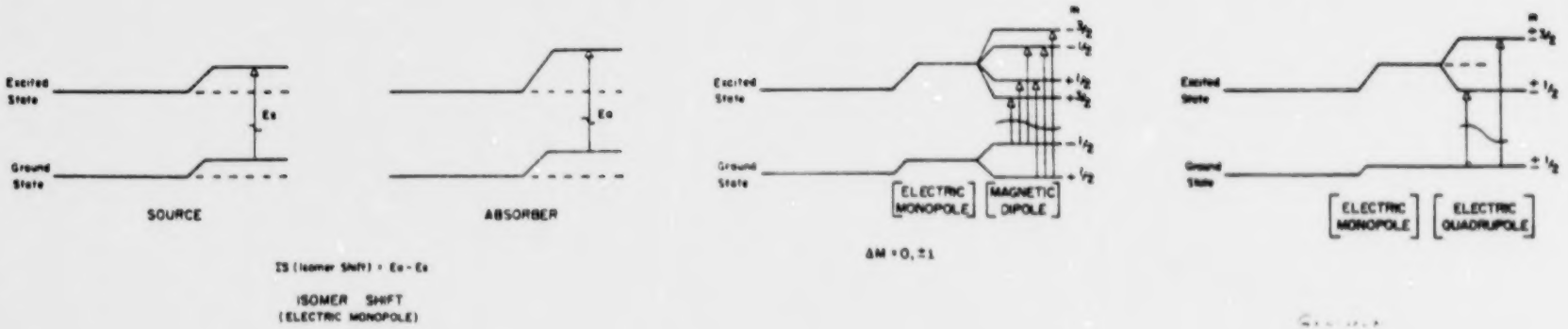


Figure 3 - A schematic diagram of the interactions between nuclear energy levels and environmental electromagnetic fields. Fe^{57} states are used.

atom's own electrons distort this electric field gradient at the nucleus and do tend to create an electric field gradient of their own. This self-generating electric-field gradient tends to amplify in many cases the effect of the more distant charges; this is known as the anti-shielding effect (12). The effect of the partially filled non-spherical shells dominates over that of the distant charges; this the electric-field gradient is a sensitive measure of these effects.

Thus the Mössbauer effect experiments allow the study of the s electron density at the nucleus, the magnitude of the electric fields at the nucleus and the magnitude of the electric field gradients at the nucleus. These fields may be calculated, approximately, using well known crystal structures and somewhat complicated but straightforward electrostatic and electromagnetic calculations. The effects of self-shielding of the individual atoms is difficult to determine. A diagram of the various interactions is shown in Figure 3.

EXPERIMENTAL EQUIPMENT USED FOR THE MÖSSBAUER EFFECT

The experimental techniques used to obtain Mössbauer effect data require the moving of the source with respect to an absorber at a velocity of the order of a centimetre per second. A velocity of 0.3 mm per second corresponds to a Doppler shift in the energy of the gamma ray of 10^{-11} times its energy. The spectrum required is: counting rate versus velocity, where the velocity is proportional to the energy. A photograph of a

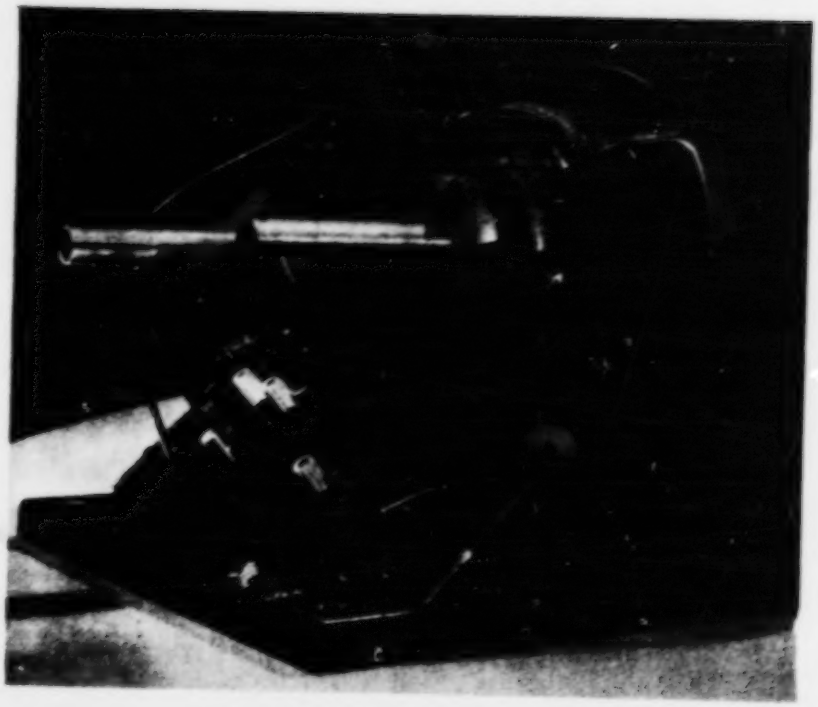


Figure 4 - A constant acceleration Mössbauer velocity drive. The source is fastened to the cone and the LVsyn projects from the rear at the speaker.

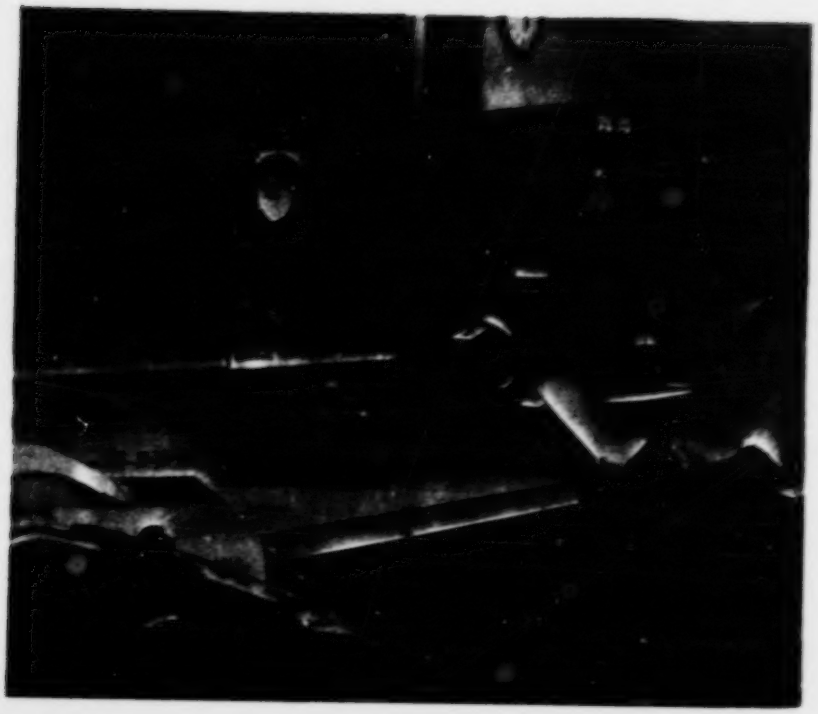


Figure 5 - Mössbauer experimental arrangement at the Department of Mines and Technical Surveys, Ottawa. A) Loudspeaker Drive, B) Pulse-Height Analysis Equipment, C) Electronics for Loudspeaker, D) On-Line Computer for Data Acquisition, E) Oscilloscope displaying a Spectrum, F) Programs used for Mössbauer Effect.

typical Mössbauer velocity drive is shown in Figure 4. The loudspeaker (13) is driven by a parabolic waveform of a frequency about eight cycles per second. The velocity of the loudspeaker cone (and hence the source) sweeps linearily, at the driving frequency, from a maximum negative value to a maximum positive value. The source thus has a constant acceleration. The velocity and counting rate information are fed into a multichannel analyser (14) or a small on-line computer (15) operated as an analyser and the data is accumulated. Figure 5 is a photograph of the system used in our laboratory.

Another technique is to use a constant velocity drive and to scan the velocity spectrum point by point. This has the advantage of requiring the taking of data at only those points required for the experiment (16). A distinct disadvantage to this type of system is that the various velocity points are taken at widely different times and the relative counting rate is subject to drift in the efficiency of the electronics. The system for detecting the radiation is determined by the nature of the isotope under study and, typically, scintillation and proportional counters are used, although the use of solid-state detectors is becoming more and more widespread.

In the constant acceleration velocity drive, the zero of velocity and the velocity scale are, in general, determined from the well known hyperfine structure of iron as shown in Figure 6. An iron source is attached to the loud-speaker drive as well as the source used for study and initial

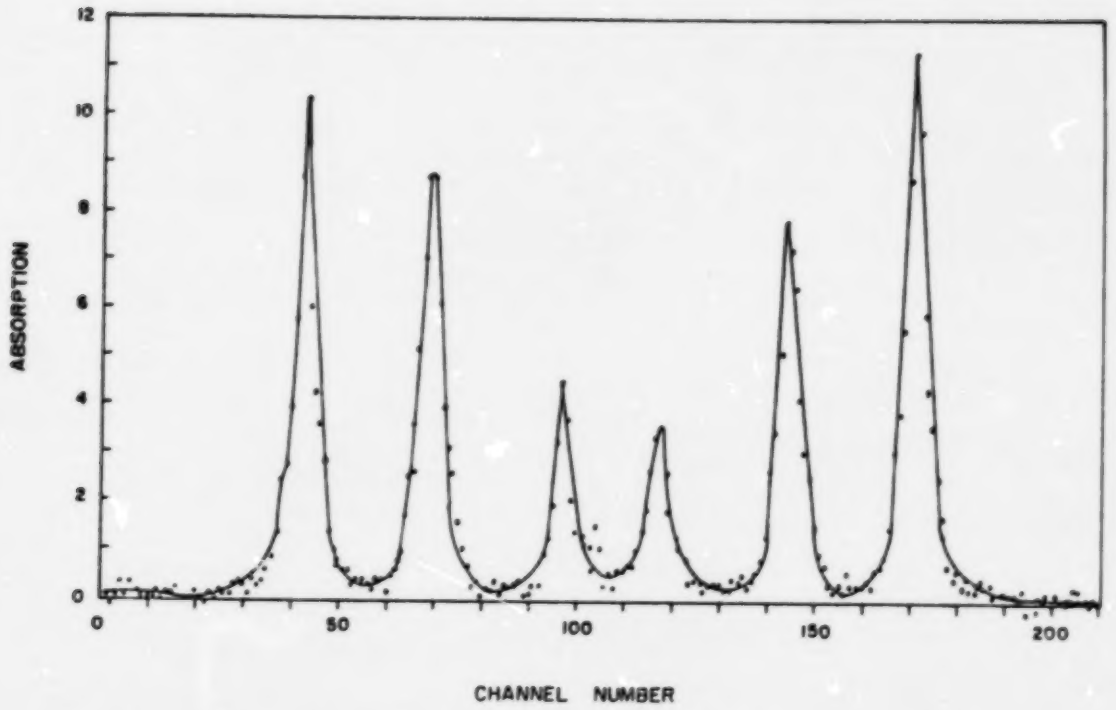


Figure 6 - Iron calibration spectrum.

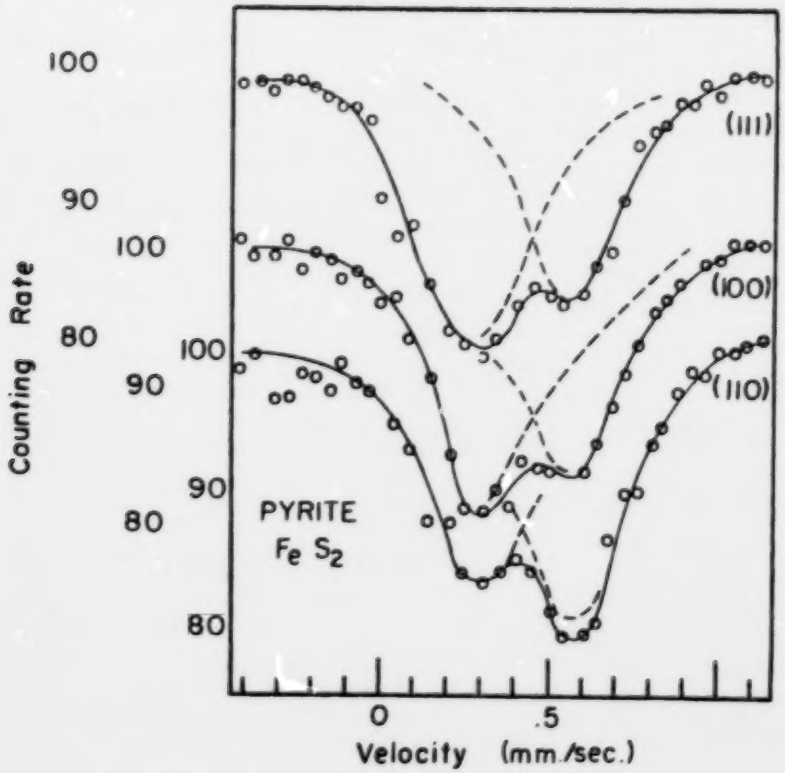


Figure 7 - Mössbauer spectra of iron pyrite.

calibrations are taken using the hyperfine structure of the iron.

MÖSSBAUER EFFECT ISOTOPES

The use of the Mössbauer effect in the study of the properties of solid state has one serious limitation - only a limited number of nuclides exhibit the Mössbauer effect. As can be seen from the expression for recoil energy, equation 1, the energy of the gamma ray must be relatively low - less than 150 keV - in order to have a small recoil, and, the lifetime of the state must be relatively long in order to achieve a relatively good energy resolution. However, if the lifetime of the state is too long, certain practical difficulties with experimental procedure occur.

The most common isotope used for Mössbauer studies is Fe^{57} which is obtained from the decay of Co^{57}. This has a 270-day half-life and a relatively high recoilless fraction at room temperature. Two other commonly used isotopes are those of Sn and Au. Most of the isotopes used for Mössbauer effect studies are obtained from radioactive decay processes but recently both neutron capture (17) and Coulomb excitation (18) have been used to excite the Mössbauer states of K^{40}. The properties of several unstable rare gas compounds have been studied using the Mössbauer techniques in both Xe and Kr (19). One of the highest resolution isotopes is Zn^{67}. This isotope has a line width of 5×10^{-14} eV, corresponding to a velocity

of 1.56×10^{-4} mm per second, which is the growth rate of a typical plant. Most rare-earth isotopes exhibit Mössbauer effect as do many of the platinum group metals.

A STUDY OF IRON PYRITE

To illustrate the information that is obtained from a Mössbauer effect experiment on a typical mineral, the work in this laboratory on iron pyrite has been chosen. Mössbauer effect spectra at room temperature of the iron states in iron pyrite, FeS_2, as a function of crystal orientation have been studied. The following features of the spectra obtained in this study, shown in Figure 7, are noteworthy: the spectra are not symmetric about zero velocity; the shape of the spectra are a function of crystal orientation; and there is a quadrupole splitting. The isomer shift of 0.3 mm per second as compared with iron metal indicates that the iron may be in a ferric (Fe^{3+}) state (Figure 8). The orientation dependence - analyzed as shown in Figure 9 - indicates that the electric field gradient lies along the (111) axis of the crystal. The quadrupole splitting of 0.30 mm per second is small indicating a self-shielding effect of the sulphur dumbell which implies that at a distance the sulphur dumbell behaves as a small effective charge center.

Thus the information obtained directly from the Mössbauer spectra is that the iron (if ionically bound) is in a ferric state and that the electric field gradient is symmetric

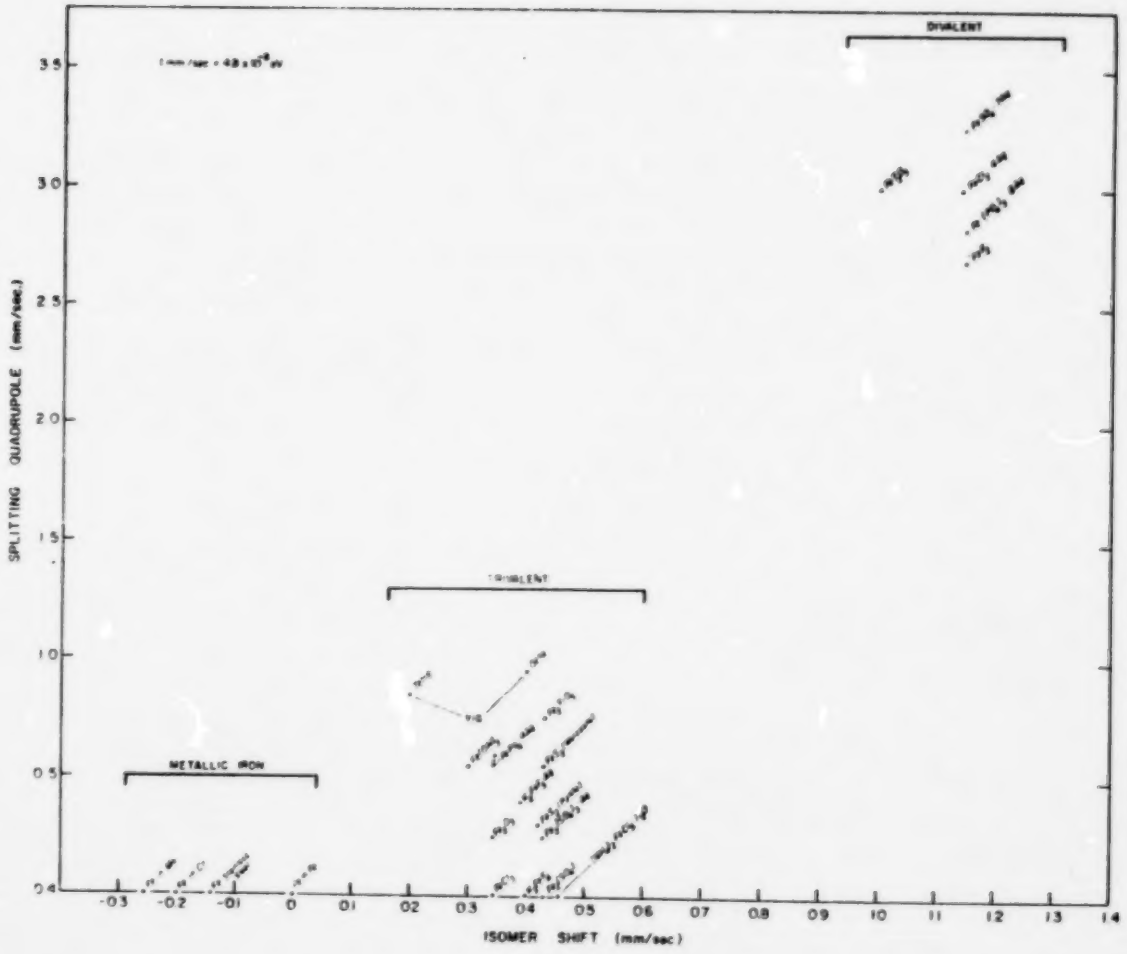


Figure 8 - A plot of isomer shift versus quadrupole splitting for various iron-containing compounds.

around the (111) axis. The small electric field gradient as shown by the relatively small quadupole splitting, indicates that the sulphur dumbell does not contribute extensively to the charge at the iron nucleus. Undoubtedly, the affect is due to the shape of the sulphur dipole rather than to self-shielding effects in the iron.

This example illustrates typical information obtainable from a Mössbauer effect study, which, together with other properties of the crystal, may be used to obtain an understanding of the material.

The Mössbauer effect combines the techniques of nuclear physics and the properties of lattice vibrations to study the internal fields of matter. It is a useful probe for studying s electron density and the magnetic and electric fields present at the nucleus. The limitation of these techniques is that because there is only a certain number of isotopes that exhibit a Mössbauer effect, only certain materials can be studied. Similar data is obtainable from NMR (Nuclear Magnetic Resonance) and NQR (Nuclear Quadrupole Resonance) studies; however both of these require external magnetic or electric fields whereas the Mossbauer effect is a zero-field experiment.

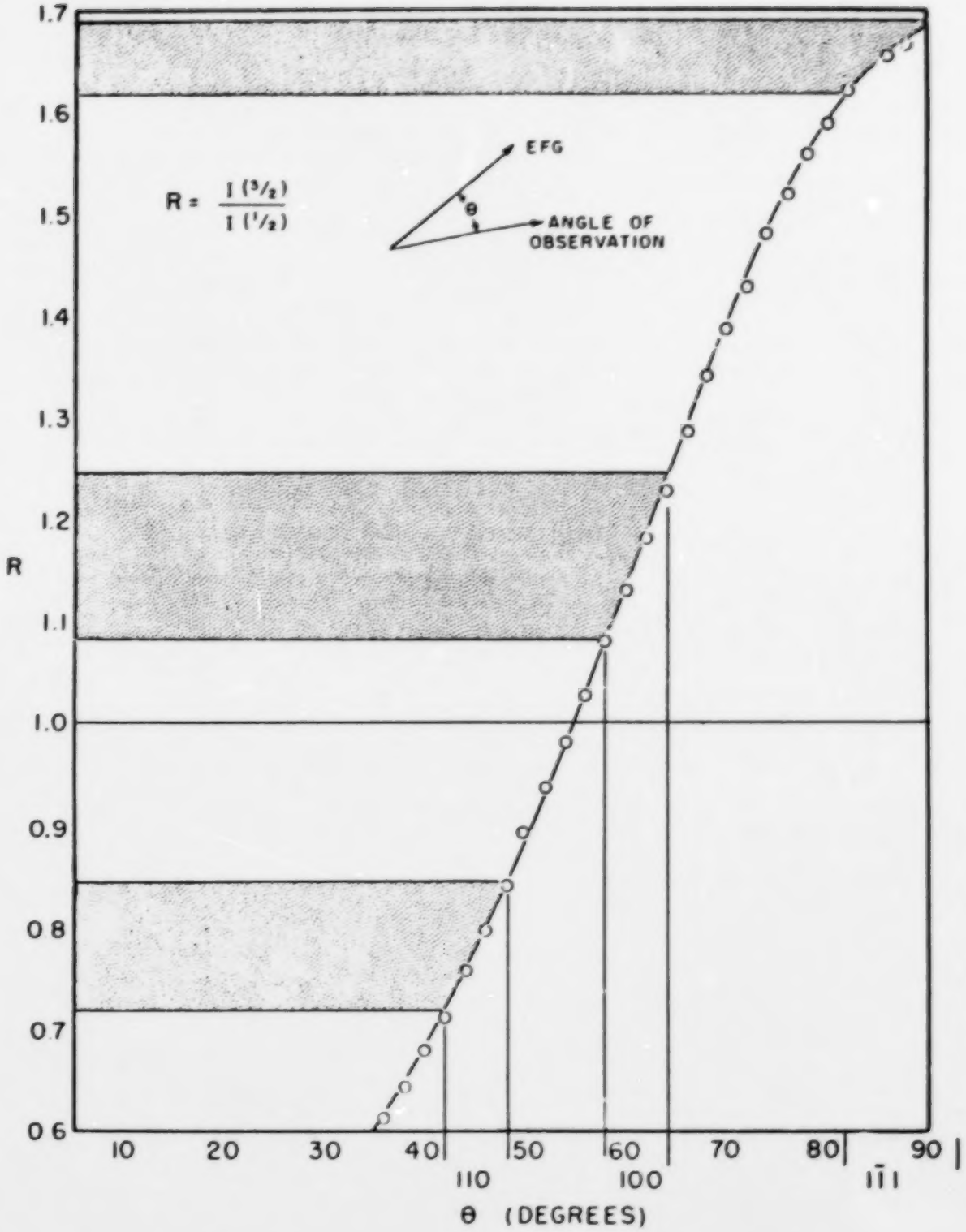


Figure 9 - The asymmetry factor for the Fe^{57} Mössbauer spectra.

REFERENCES

1. Karlsson, E., Matthais, E., Siegbahn, K., Perturbed Angular Correlations (North Holland Publishing Co., Amsterdam 1964).

2. Stewart, A.T., Kusmiss, J.H., and March, R.H., Phys. Rev. 132, 495 (1963).

3. Mössbauer, R.L., Z. Physik, 151, 124 (1958).

4. Malmfors, K.G., Beta- and Gamma-Ray Spectroscopy, 521-530, (North Holland Publishing Co., Amsterdam 1955).

5. Bunberry, D. St. P., Elliott, J.A., Hall, H.E., and Williams, J.M., Phys. Lett. 6, 34 (1963).

6. Zory, P., Phys. Rev. 140, A1401 (1965).

7. Shirley, D.A., Rev. Mod. Phys. 36, 339 (1964).

8. Wertheim, G.K., and Herber, R.H., J. Chem. Phys. 38, 2106 (1963).

9. Boyle, A.J.F. et al, Proc. Phys. Soc. London, 77, 129 (1961).

10. Cohen, R.L., Phys. Lett. 5, 177 (1963).

11. Cohen, R.L., Phys. Rev. 134, A94 (1964).

12. Sternheimer, R.M., and Foley, H.M., Phys. Rev. 92, 1460 (1953).

13. Cohen, R.L., McMullin, P.G., Wertheim, G.K., Rev. Sci. Insts., 34, 671 (1963).

14. Kankeleit, E., Rev. Sci. Insts. 35, 194 (1964).

15. Goodman, R.H., and Richardson, J.E., The Use of a Small On-Line Computer for Mössbauer Experiments, Rev. Sci. Insts. (in press) (see also Spring 1965 DECUS, 21).

16. Flinn, P.A., Rev. Sci. Insts. 34, 1422 (1963).

17. Hafemeister, D.W., and Shera, E.B., Phys. Rev. Lett. 14, 593 (1965).

18. Ruby, S.L., and Holland, R.E., Phys. Rev. Lett., 14, 591 (1965).

19. Perlow, G.J., and Perlow, M.R., Rev. Mod. Phys. 36, 353 (1964).

REVIEW ARTICLES AND BOOKS

1. Frauenfelder, H., "The Mössbauer Effect" (W.A. Benjamin Inc., New York 1962).

2. Wertheim, G.K., Science 144, 253 (1964).

3. Goldanskii, V.I., "The Mössbauer Effect and its Applications in Chemistry" (Consultants Bureau, New York 1964).

4. Abragam, A., "L'Effect Mössbauer", (Gordon and Breach, New York 1963).

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CAPTIONS

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